

## 07-Crystallography of Organometallic and Coordination Compounds

Our artificial approach consists of using metals with their different assembling properties (depending on the metal, its oxidation state, coordination number,  $d^n$  configuration, etc.) for creation of novel architectures in coordination chemistry. By an appropriate use of coordination geometry around a transition metal, binding cavities of different size between two adjacent sugar units can be planned. The structure of  $[V(DAGO)_6Na_3]$  (DAGO = 1,2:5,6 di-O-isopropylidene- $\alpha$ -D-gluco-furanose) exemplifies the complexation of ion-pairs (Figure 1); six sugar moieties are octahedrally arranged around the vanadium atom and in three of the cavities created by pairs of sugars sodium ions are located at distances Na---O ranging from 2.24 to 2.94 Å.

Sugars can be used as ancillary ligands in the case of functionalizable centers in organometallic chemistry. The structure of the unprecedented homoleptic compound of formula  $[Mo_2(DAGO)_6]$  containing a triple Mo=Mo (2.218 Å) bond is shown in Figure 2. Each Mo atom binds three sugars via their exocyclic oxygen atoms and are arranged around each Mo in such a way that bonds Mo-O form a calix with the Mo-Mo bond as stem.

Sugars act also as chelating ligands with alkali metals via oxygen atoms. Figure 3 shows the new structure of  $[Li(DAGO)]_4$  with a cubic cage of four lithium atoms and four oxygen atoms, which occupy alternatively the vertices of the cube.

Figure 1

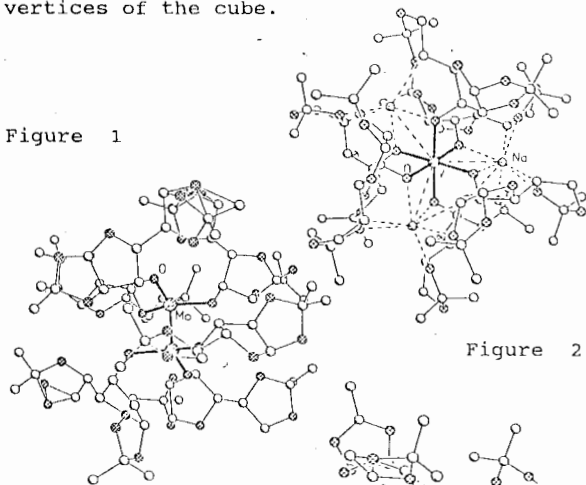


Figure 2

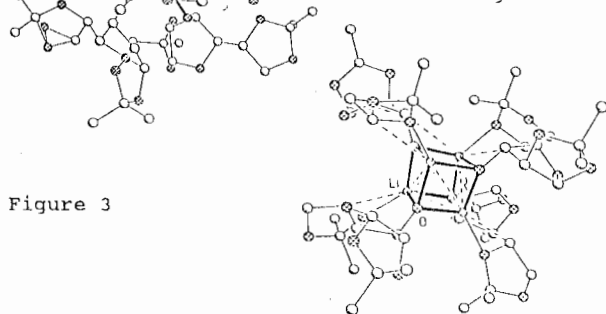
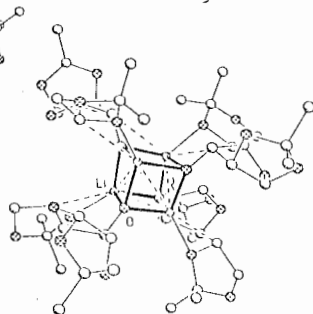
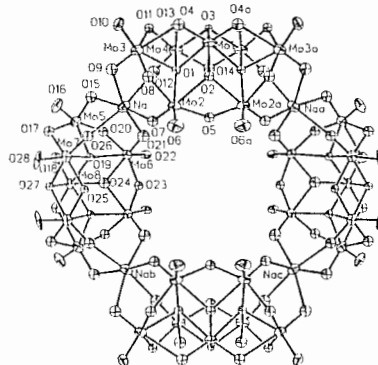


Figure 3

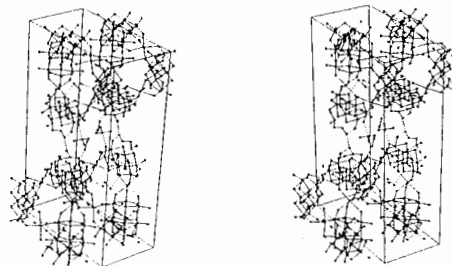


**PS-07.03.11** A CYCLIC COMPLEX FORMED BY SODIUM AND HEPTAMOLYBDATE IONS: THE CRYSTAL STRUCTURE OF  $(C_6H_{12}NO)_5(NH_4)_4[Na_4Mo_{28}O_{96}] \cdot 6CH_3OH$ . By R. Hämäläinen\* and U. Turpeinen, Department of Chemistry, P.O. Box 6, Vuorikatu 20, FIN-00014 University of Helsinki, Finland.

Colorless crystals of the title compound were obtained by slow evaporation of a methanol solution containing ammoniumparamolybdate, 2-dimethylaminoethanol, sodium hydroxide and  $NH_3$ . The crystal used for data collection had approximate dimensions 0.1 x 0.1 x 0.2 mm and was sealed in a capillary. Crystal data for the title compound:  $M=5300.0$ , orthorhombic space group  $Pm\bar{m}n$  with  $a=22.275(6)$ ,  $b=36.758(9)$ ,  $c=11.059(6)$  Å,  $Z=2$ ,  $V=9055(4)$  Å<sup>3</sup>,  $\rho(MoK\alpha)=1.96$  mm<sup>-1</sup>,  $F(000)=5112$ ,  $\lambda(MoK\alpha)=0.71069$  Å,  $d_{obs}=1.95$  Mgm<sup>-3</sup> and  $d_{calc}=1.944$  Mgm<sup>-3</sup>. The structure was solved by Patterson and Fourier methods using the program system SHELXTL-Plus (Sheldrick, 1990) and refined with anisotropic temperature factors for the Mo, Na and terminal O atoms of the anion group and isotropic factors for the other atoms. Hydrogen atoms were not determined. Final  $R=0.078$ ,  $R_w=0.085$  and  $S=1.19$ .



The configuration and the interatomic distances of the heptamolybdate group  $[Mo_7O_{24}]^{6-}$  are essentially those found earlier in  $M_6[Mo_7O_{24}] \cdot 4H_2O$  ( $M=NH_4$  or  $K$ ) (Evans, H.T., Gatehouse, B.M. & Leverett, P. (1975). *J.C.S. Dalton*, 505-514.) The sodium ions are six-coordinated with Na-O distances of 2.41(4) - 2.48(4) Å and with coordination angles between 81.3(12) and 97.4(13)°. The complex structure is stabilized by a set of hydrogen bonds involving  $[Na_4Mo_{28}O_{96}]^{20-}$  complex anions, methanol molecules, ammonium and dimethyl-(2-hydroxyethyl)ammonium cations.



Stereoscopic view of the unit cell.

**PS-07.03.12** THE CRYSTAL STRUCTURE OF 2-DIMETHYLAMINOETHANOLATO BRIDGED TETRANUCLEAR COPPER(II) 4-CHLOROBENZOATO COMPLEX:  $[Cu_4(C_7H_4ClO_2)_4(C_4H_10NO)_4] \cdot 2CH_3OH$ . By U. Turpeinen\*, R. Hämäläinen and I. Mutikainen, Department of Chemistry, P.O. Box 6, Vuorikatu 20, FIN-00014 University of Helsinki, Finland.

In a systematic investigation of the reaction between Cu(II) carboxylates and 2-dialkylaminoethanols, monomeric, dimeric, tetrameric, hexameric and nonameric complexes have been synthesized and structurally characterized by X-ray crystallography (Turpeinen, U. (1985). *Finn. Chem. Lett.* 13, 73-83;

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Turpeinen, U., Hämäläinen, R. & Reedijk, J. (1987). *Inorg. Chim. Acta*, **134**, 87–93; Turpeinen, U., Hämäläinen, R. & Reedijk, J. (1988). *Inorg. Chim. Acta*, **154**, 201–207. The title compound was obtained by slow evaporation of methanol solution containing Cu(II) 4-chlorobenzoate and 2-dimethylamino-ethanol. Blue crystals of  $[\text{Cu}_4(\text{C}_7\text{H}_4\text{ClO}_2)_4(\text{C}_4\text{H}_{10}\text{NO})_4] \cdot 2\text{CH}_3\text{OH}$  are triclinic, space group  $P\bar{1}$ ,  $a=14.056(4)$ ,  $b=14.704(4)$ ,  $c=15.335(3)$  Å,  $\alpha=106.27(2)$ ,  $\beta=105.76(2)$ ,  $\gamma=102.24(2)^\circ$ ,  $Z=2$ ,  $V=2782(1)$  Å<sup>3</sup>,  $D_x=1.495$  Mg m<sup>-3</sup>,  $M_r=1293.1$ , final R value 0.039 for 5563 significant reflections.

The structure consists of discrete molecules. The Cu and bridging ethanolato O atoms form a cubane-type  $\text{Cu}_4\text{O}_4$  core in which the short Cu–O bonds form an eight-membered ring folded in a boat-like conformation.

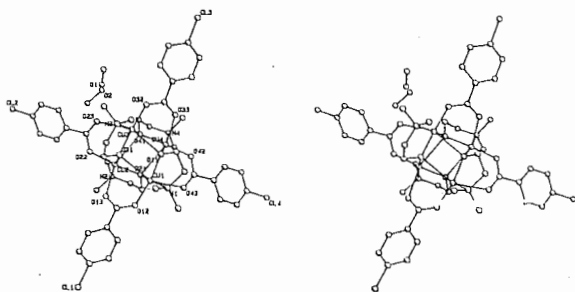


Fig. 1. Stereoview of the molecule.

Within the  $\text{Cu}_4\text{O}_4$  core the long Cu–Cu distances are 3.664 and 3.796 Å and the four short Cu–Cu distances range from 3.096 to 3.191 Å. Each Cu atom is surrounded by two ethanolato oxygen atoms, a carboxyl oxygen atom and an amino nitrogen atom in a nearly square-planar arrangement with average Cu–O and Cu–N bonds of 1.936 and 2.055 Å. The axial sites of each Cu atom are occupied by an ethanolato oxygen and an oxygen atom of the carboxylate group with Cu–O distances of 2.409–2.815 Å.

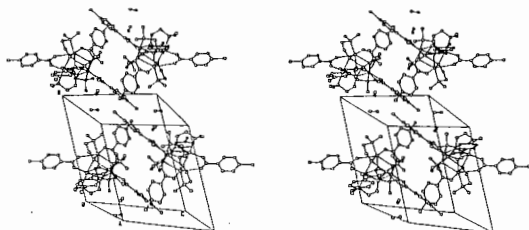


Fig. 2. Stereoscopic view of the packing.

**PS-07.03.13 CRYSTAL STRUCTURE OF A TRINUCLEAR SULFIDOTUNGSTATE ANION.** By Masood Parvez\*, P. Michael Boorman and Meiping Wang, Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4.

We have been exploring the controlled polymerization of  $\text{WS}_4^{2-}$  anions by alkylation reactions. The  $\text{W}_3\text{S}_9^{2-}$  anion has been previously reported as a product of the reaction between  $\text{WS}_4^{2-}$  and alkyl halides. We have found that the complex  $\text{Cl}_3\text{W}(\mu\text{-SEt}_2)_3\text{WCl}_3$  (**1**) is an effective ethylating agent, and will cause the trimerization of  $\text{WS}_4^{2-}$  to  $\text{W}_3\text{S}_9^{2-}$ . From  $^1\text{H}$  NMR data we have evidence that the  $\text{W}_3\text{S}_9^{2-}$  anion can itself be alkylated, hence we wished to see if clusters of higher nuclearity could be prepared this way. One product of the reaction between **1** and  $[\text{PPh}_4]_2[\text{W}_3\text{S}_9]$  in a mixture of MeCN and N,N-dimethylformamide (DMF) was isolated and subjected to an X-ray crystal structure determination. It has been shown to be  $[\text{PPh}_4]_2[\text{S}_2\text{W}(\mu\text{-S})_2\text{W}(\text{DMF}) (\text{S}) (\mu\text{-S})_2\text{WS}_2]$ , rather than a cluster of higher nuclearity as was

anticipated. The structure has some interesting features, however, in that the sulfide and DMF ligands on the central tungsten are disordered over the two axial sites.

Crystal data.  $\text{S}_9\text{W}_3(\text{C}_3\text{H}_6\text{NO}) \cdot 2(\text{C}_{24}\text{H}_{20}\text{P})$ , monoclinic, space group  $P2_1/n$ ,  $a = 9.863(2)$ ,  $b = 14.618(3)$ ,  $c = 18.795(3)$  Å,  $\beta = 97.98(1)^\circ$ ,  $V = 2683.6(8)$  Å<sup>3</sup>,  $Z = 2$ ,  $R = 0.072$  for 3813 observed data ( $I > 3\sigma(I)$ ) collected on a Rigaku AFC6S at 150(1) K.

**PS-07.03.14 CRYSTAL STRUCTURE OF DIAMINE COMPLEXONATES OF COBALT WITH ALKALINE-EARTH CATIONS** by L.A.Zassourskaya\*, T.N.Polynova, V.B.Rybakov, M.A.Porai-Koshits. Department of Chemistry, Moscow State University, 119899, Moscow, Russia.

X-ray structure analysis and crystal chemistry investigation of  $\text{M}'[\text{ML}]_2 \cdot n\text{H}_2\text{O}$  complexonates ( $\text{M}'$ —alkaline-earth cation,  $\text{M}=\text{Co(II)}$ ,  $\text{Co(III)}$ ,  $\text{L}=(\text{edta})^{4-}$ ,  $(\text{Hedta})^{3-}$ , where edta—ethylenedia-minetetraacetic acid) were carried out in order to study the role of  $\text{M}'$  in the formation of their crystal structure. The active interaction between  $\text{M}'$  and the ligand leads to change the structural function of the complexon carboxylate groups. The interaction of  $\text{M}'$  with a single carbonyl oxygen atom leads change the structural function of the complexon carboxylate groups. The interaction of  $\text{M}'$  with a single carbonyl oxygen atom leads to the formation of an island structure. So,  $[\text{Mg}(\text{CoHedta}(\text{NO}_2))_2 \cdot 9\text{H}_2\text{O}]$  consists of heterometallic binuclear complexes  $[\text{Mg}(\text{H}_2\text{O})_5\text{CoHedta}(\text{NO}_2)]^+$  and  $[\text{CoHedta}(\text{NO}_2)]^-$  anions. If  $\text{M}'$  is connected with several carbonyl atoms chain ( $\text{Ba}(\text{Coedta})_2 \cdot 8\text{H}_2\text{O}$ ) or layer ( $\text{Ca}(\text{CoHedta}(\text{CN})_2 \cdot 6\text{H}_2\text{O})$ ) structures are formed. Even more interesting are isostructural layer compounds  $\text{M}'[\text{CoHedta}]_2 \cdot 6\text{H}_2\text{O}$ , where  $\text{M}'=\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ . Besides water molecules  $\text{M}'$  coordinates both carbonyl and carboxyl oxygen atoms forming four-membered cycles. The structure of  $\text{Ca}(\text{Coedta})_2 \cdot 7\text{H}_2\text{O}$  is the most peculiar among calcium complexonates, because in it  $\text{Ca}^{2+}$  cation is completely hydrated and therefore plays the role of "outer sphere" cation. The wide diversity in the nature of the interaction between  $\text{M}'$  and carboxylate groups makes the investigation of the compounds of such type important.

**PS-07.03.15 SYNTHESIS AND CRYSTAL STRUCTURE OF TETRACOBALT CLUSTER COMPLEX**  $[\text{Co}_4(\mu_3\text{-S})(\text{SCH}_2\text{CH}_2\text{S})_3(\text{PPh}_3)_3\text{Cl}]$ . By F. L. Jiang\*, Z. Y. Huang, B. S. Kang, M. C. Hong and H. Q. Liu, State Key Lab. of Struct. Chem. and Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

A new tetracobalt compound  $[\text{Co}_4(\mu_3\text{-S})(\text{SCH}_2\text{CH}_2\text{S})_3(\text{PPh}_3)_3\text{Cl}]$  (**1**) was prepared by reacting  $\text{CoCl}(\text{PPh}_3)_2$  and  $\text{Na}_2\text{edt}$  ( $\text{H}_2\text{edt}=1,2$  ethanedithiol) in acetonitrile, and structurally characterized by X-ray diffraction methods. Compound **1** crystallizes in the trigonal space group  $P\bar{3}$  with  $a=16.505(8)$ ,  $c=13.401(6)$  Å,  $V=3162(3)$  Å<sup>3</sup>,  $Z=2$  and  $R(\text{w})=0.046$  (0.064) for 2636 reflections ( $I > 3\sigma(I)$ ). The cluster contains four cobalt atoms in the form of a trigonal pyramid. The basal  $\text{Co}_3$  triangle is capped by  $\mu_3\text{-S}(3)$  below, and also di-bridged by  $\text{S}(2)$  of  $\text{edt}^{2-}$  in each edge of the triangle, while the triangle is bridged to the apical  $\text{Co}(2)$  above by another